

DECLARATION

I, Kyoko Fujimoto of c/o SHIGA INTERNATIONAL PATENT OFFICE, GranTokyo South Tower 1-9-2, Marunouchi, Chiyoda-ku, Tokyo 100-6620 JAPAN, understand both English and Japanese, am the translator of the English document attached, and do hereby declare and state that the attached English document contains an accurate translation of Claims and Specification of Japanese Patent Application No. 2004-045043 and that all statements made herein are true to the best of my knowledge.

I further declare that all statements made herein to our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date

October 7, 2010

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Kyoko Fujimoto

JAPAN PATENT OFFICE

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Applicant(s): Tokyo Ohka Kogyo Co., Ltd.

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Commissioner,

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[List of Materials Being Submitted]

[Name of Material] Scope of claims for patent 1
[Name of Material] Specification 1
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[Name of Document] Scope of claims for patent

[Claim 1]

A base material for a pattern-forming material, comprising a protected material (X1), which is formed from a polyhydric phenol compound (x) that comprises two or more phenolic hydroxyl groups and has a molecular weight within a range from 300 to 2,500, in which either a portion of, or all of, said phenolic hydroxyl groups are protected with acid dissociable, dissolution inhibiting groups, wherein a proportion within said base material of an unprotected material (X2), in which said phenolic hydroxyl groups of said polyhydric phenol compound (x) are not protected with acid dissociable, dissolution inhibiting groups, is no more than 60% by weight.

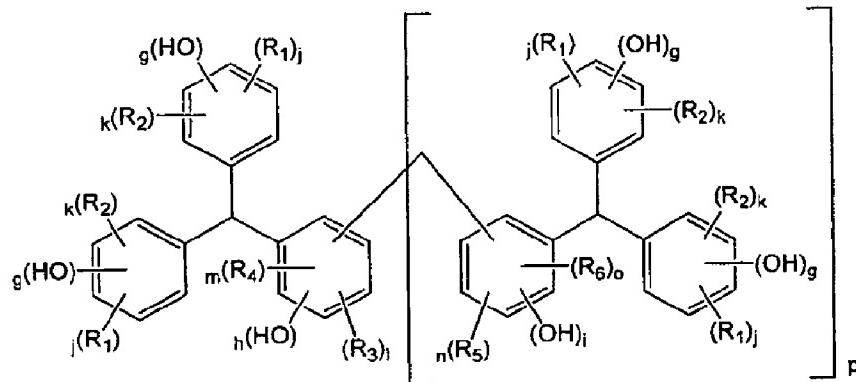
[Claim2]

A base material for a pattern-forming material according to claim 1, wherein a molecular weight dispersity (M_w/M_n) of said polyhydric phenol compound (x) is no more than 1.5.

[Claim3]

A base material for a pattern-forming material according to claim 1 or 2, wherein said polyhydric phenol compound (x) is a compound represented by a general formula (I) shown below:

[Formula 1]



[wherein, R_1 through R_6 each represent, independently, an alkyl group or aromatic hydrocarbon group of 1 to 10 carbon atoms, and these structures may also include a hetero atom; g and j each represent, independently, an integer of 1 or greater, k represents

either 0 or an integer of 1 or greater, and g+j+k is no greater than 5; h is an integer of 1 or greater, l and m each represent, independently, either 0 or an integer of 1 or greater, and h+l+m is no greater than 4; i is an integer of 1 or greater, n and o each represent, independently, either 0 or an integer of 1 or greater, and i+n+o is no greater than 4; and p is either 0 or 1].

[Claim4]

A positive resist composition, comprising a base material component (A), which contains acid dissociable, dissolution inhibiting groups and displays increased alkali solubility under action of acid, and (B) an acid generator that generates acid on exposure, wherein

said base material component (A) is a base material for a pattern-forming material according to any one of claims 1 to 3.

[Claim5]

A positive resist composition according to claim 4, further comprising a nitrogen-containing organic compound (D).

[Claim6]

A method of forming a resist pattern comprising the steps of applying a positive resist composition according to claim 4 or 5 to a substrate, conducting a prebake, performing selective exposure, conducting PEB (post exposure baking), and performing alkali developing to form a resist pattern.

[Name of Document] Specification

[Name of Invention] BASE MATERIAL FOR PATTERN-FORMING MATERIAL,
POSITIVE RESIST COMPOSITION AND METHOD OF RESIST PATTERN
FORMATION

[Technical Field]

[0001]

The present invention relates to base material for a pattern-forming material, a positive resist composition, and a method of resist pattern formation.

[Background Art]

[0002]

In recent years, in the production of semiconductor elements and liquid crystal display elements, advances in lithography techniques have lead to rapid progress in the field of pattern miniaturization. Typically, these miniaturization techniques involve shortening the wavelength of the exposure light source. Conventionally, ultraviolet radiation such as g-line and i-line radiation has been used, but nowadays, mass production of semiconductor elements using KrF excimer lasers and ArF excimer lasers has already commenced. Investigations are also being conducted into the use of even shorter wavelength sources than the above excimer lasers, including F₂ excimer lasers, electron beams, extreme ultraviolet radiation, and X-rays.

Furthermore, one example of a pattern-forming material capable of forming a pattern of minute dimensions is a chemically amplified resist, which includes a base material component with a film-forming capability, and an acid generator component that generates acid on exposure. Chemically amplified resists include negative compositions, which undergo a reduction in alkali solubility on exposure, and positive compositions, which display increased alkali solubility on exposure.

Conventionally, the most common base material components used within pattern-forming materials such as resists are polymers with a weight average molecular weight of at least 5,000.

[0003]

However, when a pattern is formed using this type of pattern-forming material, a problem arises in that roughness can develop on the upper surface and side wall surfaces of the pattern.

This type of roughness has conventionally posed few problems. However in recent years, with the rapid miniaturization of semiconductor elements and the like, ever higher levels of resolution such as width dimensions of no more than 90 nm are being demanded, and this miniaturization has meant that roughness is becoming a more serious problem. For example, when a line pattern is formed, roughness on the side wall surfaces of the pattern known as LER (line edge roughness) causes fluctuation in the line width that is formed, and although the degree of this fluctuation in the line width is preferably suppressed to no more than approximately 10% of the width dimension, the effects of LER increase as the pattern dimensions are reduced. For example, when a line pattern with dimensions of approximately 90 nm is formed, the degree of the fluctuation in the line width is preferably suppressed to no more than approximately 10 nm.

However, the polymers typically used as base materials have a large root mean squared radius per molecule of several nm, meaning the degree of fluctuation described above is equivalent to the width of only a few polymer molecules. As a result, as long as polymers are used as the base material component, reductions in LER will remain extremely difficult to achieve.

[0004]

On the other hand, the use of low molecular weight materials containing alkali-soluble groups such as hydroxyl groups, wherein either a portion of, or all of, the hydroxyl groups are protected with acid dissociable, dissolution inhibiting groups, as the base material has also been proposed (for example, see patent references 1 and 2). These low molecular weight materials have small root mean squared radius values as a result of their lower molecular weight, and as such, their contribution to LER is expected to be minimal.

[Patent Reference 1]

Japanese Unexamined Patent Application, First Publication No. 2002-099088

[Patent Reference 2]

Japanese Unexamined Patent Application, First Publication No. 2002-099089

[Disclosure of the Invention]

[Problems to be solved by the Invention]

[0005]

However, even when these low molecular weight materials are used, satisfactory improvement in the level of LER is still difficult to achieve, and further improvements in the level of LER are still sought.

The present invention takes the above circumstances into consideration, with an object of providing a base material for a pattern-forming material, a positive resist composition, and a method of resist pattern formation that are capable of forming a pattern with reduced levels of LER.

[Means to Solve the Problems]

[0006]

When the inventors of the present invention undertook further investigation focused on the base material for a pattern-forming material containing a protected material in which the phenolic hydroxyl groups of a polyhydric phenol compound with a specific low molecular weight are protected with acid dissociable, dissolution inhibiting groups, they discovered that the object above could be achieved by ensuring that the proportion of unprotected material, in which none of the hydroxyl groups of the polyhydric phenol compound are protected with acid dissociable, dissolution inhibiting groups, is suppressed to no more than a specific value, and they were thus able to complete the present invention.

In other words, a first aspect of the present invention is a base material for a pattern-forming material that includes a protected material (X1), which is formed from a polyhydric phenol compound (x) that contains two or more phenolic hydroxyl groups and has a molecular weight within a range from 300 to 2,500, in which either a portion of, or all of, the phenolic hydroxyl groups are protected with acid dissociable, dissolution inhibiting groups, wherein the proportion within the base material of an unprotected material (X2), in which the phenolic hydroxyl groups of the polyhydric phenol compound (y) are not protected with acid dissociable, dissolution inhibiting groups, is no more than 60% by weight.

Furthermore, a second aspect of the present invention is a positive resist composition that includes a base material component (A), which contains acid dissociable, dissolution inhibiting groups and displays increased alkali solubility under the action of acid, and (B) an acid generator that generates acid on exposure, wherein

the base material component (A) is the base material for the pattern-forming material.

Furthermore, a third aspect of the present invention is a method of forming a resist pattern that includes the steps of applying the positive resist composition according to the second aspect to a substrate, conducting a prebake, performing selective exposure, conducting PEB (post exposure baking), and performing alkali developing to form the resist pattern.

[0007]

In this description, the term "exposure" refers to irradiation with some form of radiation, or direct patterning or irradiation with an electron beam.

[Effect of the Invention]

[0008]

A base material for a pattern-forming material, a positive resist composition, and a method of forming a resist pattern according to the present invention enable the formation of a high resolution pattern with a reduced level of LER.

[Best Mode for Carrying Out the Invention]

[0009]

As follows is a more detailed description of the present invention.

<Base Material for Pattern-forming Material>

A base material for a pattern-forming material of the present invention is a base material for a pattern-forming material that includes a protected material (X1), which is formed from a polyhydric phenol compound (x) that contains two or more phenolic hydroxyl groups and has a molecular weight within a range from 300 to 2,500, in which either a portion of, or all of, the phenolic hydroxyl groups are protected with acid dissociable, dissolution inhibiting groups, wherein the proportion within the base material of an unprotected material (X2), in which the phenolic hydroxyl groups of the polyhydric phenol compound (y) are not protected with acid dissociable, dissolution inhibiting groups, is no more than 60% by weight.

In this description, the polyhydric phenol compound (x) refers to the compound prior to protection with the acid dissociable, dissolution inhibiting groups, the compound that has been protected with acid dissociable, dissolution inhibiting groups is referred to as the protected material (X1), and the compound that has not been protected is referred

to as the unprotected material (X2), and the base material for a pattern-forming material according to the present invention includes the protected material (X1) and must contain no more than 60% by weight of the unprotected material (X2).

[0010]

<Polyhydric Phenol Compound (x)>

There are no particular restrictions on the polyhydric phenol compound (x) used in the formation of the protected material and the unprotected material, provided the compound contains two or more phenolic hydroxyl groups, has a molecular weight within a range from 300 to 2,500, , and examples of suitable compounds include the polyhydric phenol compounds known as sensitizers or heat resistance improvement agents for non-chemically amplified g-line or i-line resists. Specific examples of these polyhydric phenols include the compounds listed below:

bis(2,3,4-trihydroxyphenyl)methane, 2-(4-hydroxyphenyl)-2-(4'-hydroxyphenyl)propane, 2-(2,3,4-trihydroxyphenyl)-2-(2',3',4'-trihydroxyphenyl)propane, bis(4-hydroxy-3,5-dimethylphenyl)-2-hydroxyphenylmethane, bis(4-hydroxy-3,5-dimethylphenyl)-4-hydroxyphenylmethane, bis(4-hydroxy-2,5-dimethylphenyl)-2-hydroxyphenylmethane, bis(4-hydroxy-3,5-dimethylphenyl)-3,4-dihydroxyphenylmethane, bis(4-hydroxy-2,5-dimethylphenyl)-3,4-dihydroxyphenylmethane, bis(4-hydroxy-3-methylphenyl)-3,4-dihydroxyphenylmethane, bis(4-hydroxy-3-methylphenyl)-2-hydroxyphenylmethane, bis(3-cyclohexyl-4-hydroxy-6-methylphenyl)-2-hydroxyphenylmethane, bis(3-cyclohexyl-4-hydroxy-6-methylphenyl)-3,4-dihydroxyphenylmethane, bis(4-hydroxy-3,5-dimethylphenyl)-2-hydroxyphenylmethane, bis(4-hydroxy-2,3,5-trimethylphenyl)-2-hydroxyphenylmethane, bis(4-hydroxy-2,3,5-trimethylphenyl)-3-hydroxyphenylmethane, bis(4-hydroxy-2,3,5-trimethylphenyl)-4-hydroxyphenylmethane, 1-[1-(4-hydroxyphenyl)isopropyl]-4-[1,1-bis(4-hydroxyphenyl)ethyl]benzene, and four-benzene ring compounds of formalin condensation products of phenols such as phenol, m-cresol, p-cresol and xylenol.

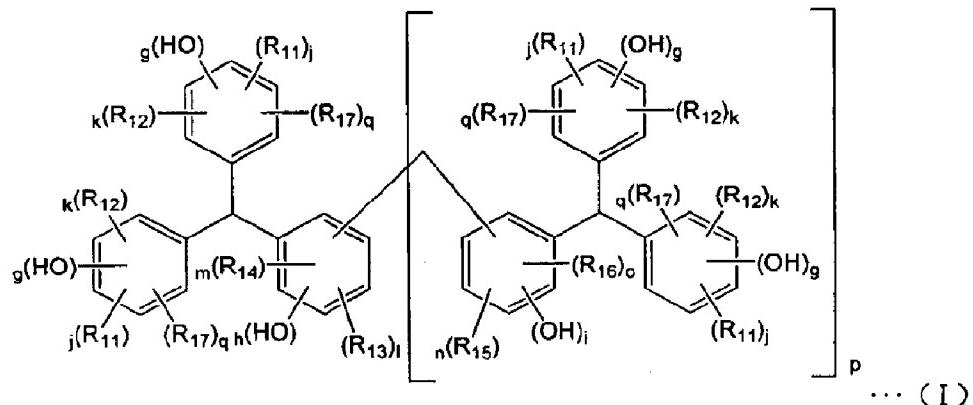
[0011]

In particular, in the present invention, the polyhydric phenol compound (x) is preferably a polyhydric phenol compound represented by the general formulas (I) shown

below, as such compound exhibits excellent manifestation of the effects of the present invention.

[0012]

[Formula 1]



[0013]

In the above formula, R₁ through R₆ each represent, independently, a straight-chain, branched, or cyclic lower alkyl group of 1 to 10 carbon atoms, and even more preferably 1 to 5 carbon atoms, a cyclic alkyl group of 5 to 6 carbon atoms, or an aromatic hydrocarbon group. These alkyl groups or aromatic hydrocarbon groups may include a hetero atom such as an oxygen atom, nitrogen atom, or sulfur atom within the structure. Specific examples of suitable aromatic hydrocarbon groups include a phenyl group, tolyl group, xylyl group, mesityl group, phenethyl group, or naphthyl group.

g and j each represent, independently, an integer of 1 or greater, and preferably an integer from 1 to 2, k represents either 0 or an integer of 1 or greater, and preferably an integer that does not exceed 2, and g+j+k is no greater than 5.

h is an integer of 1 or greater, and preferably from 1 to 2, l and m each represent, independently, either 0 or an integer of 1 or greater, and preferably an integer that does not exceed 2, and h+l+m is no greater than 4.

i is an integer of 1 or greater, and preferably from 1 to 2, n and o each represent, independently, either 0 or an integer of 1 or greater, and preferably an integer that does not exceed 2, and i+n+o is no greater than 4.

p is either 0 or 1, and is preferably 1.

Of these possibilities, compounds in which R₁ is a cycloalkyl group, j is 1, R₂ is a lower alkyl group, k is 1, and g is 1 are preferred.

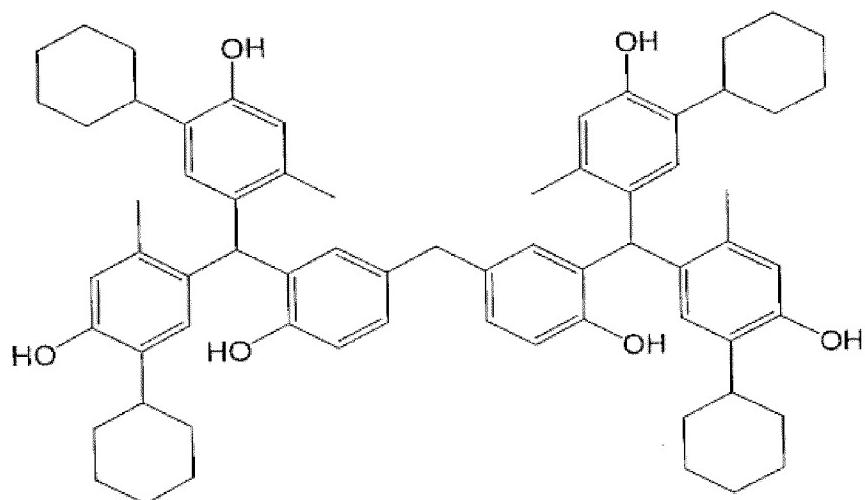
In addition, compounds in which R₁ is a cyclohexyl group, j is 1, R₁₂ is a lower alkyl group, k is 1, and g is 1, and moreover, q, l, m, n and o are zero, and h and i are both 1 enable the formation of a fine pattern with reduced LER and a high level of resolution, and are consequently preferred.

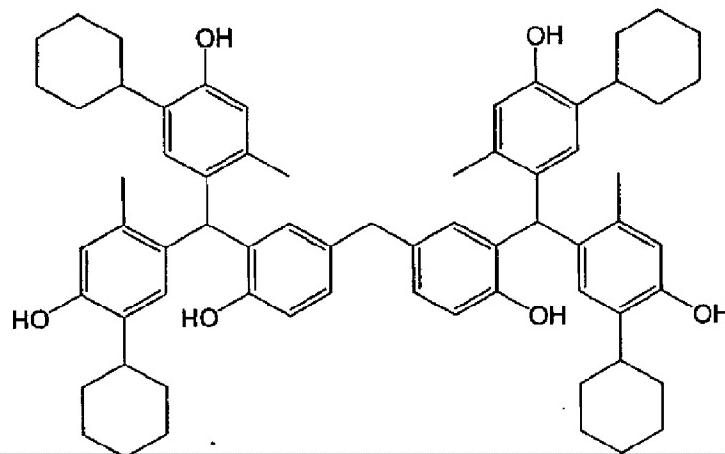
[0014]

Of the polyhydric phenol compounds represented by the above general formula (I), the most preferred compounds are the polyhydric phenol compounds represented by formulas (II) or (III) shown below.

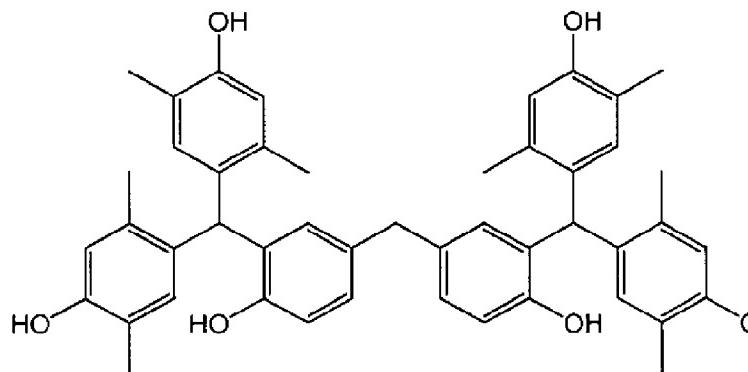
[0015]

[Formula2]





(II)



(III)

[0016]

In the present invention, the polyhydric phenol compound (x) must have a molecular weight within a range from 300 to 2,500, and this molecular weight is preferably from 450 to 1,500, and even more preferably from 500 to 1,200. By ensuring that the molecular weight is no higher than the above upper limit, an adequate LER reduction effect can be achieved. Furthermore, the resolution also improves. Furthermore, ensuring that the molecular weight is at least as large as the lower limit enables the formation of a resist pattern with a favorable profile shape.

[0017]

Furthermore, polyhydric phenol compounds (x) in which the molecular weight dispersity (M_w/M_n) is no more than 1.5 exhibit superior effects for the present invention, and are consequently preferred. It is thought that the reason for this observation is that a narrower molecular weight distribution for the polyhydric phenol compound (x) results in

comparatively uniform alkali solubility for each of the protected materials and the unprotected material. Smaller dispersity values are preferred, and the dispersity value is even more preferably no more than 1.4, and is most preferably 1.3 or smaller. In those cases where a single polyhydric phenol compound (x) is used alone in the base material, the dispersity is 1.

The dispersity can be adjusted either by removing reaction by-products and impurities following synthesis of the polyhydric phenol compound (x) that represents the targeted product, or by using conventional methods such as molecular weight fractionation treatments to remove the unneeded molecular weight fractions.

The dispersity is calculated by measuring the weight average molecular weight (M_w) and the number average molecular weight (M_n) using a typical method used for the measurement of these M_w and M_n values for a polymer, such as a gel permeation chromatography method, and then determining the M_w/M_n ratio.

[0018]

<Protected Material (X1)>

The protected material (X1) is a compound in which either a portion of, or all of, the phenolic hydroxyl groups of the polyhydric phenol compound (x) have been protected by substitution with acid dissociable, dissolution inhibiting groups.

There are no particular restrictions on the acid dissociable, dissolution inhibiting groups, and any group can be selected from amongst the various acid dissociable, dissolution inhibiting groups proposed for use within the hydroxystyrene-based resins and (meth)acrylate-based resins and the like used within conventional KrF or ArF chemically amplified resist compositions.

Specific examples of suitable groups include chain-like alkoxyalkyl groups, tertiary alkyloxycarbonyl groups, tertiary alkyl groups, tertiary alkoxy carbonylalkyl groups, and cyclic ether groups.

[0019]

Examples of suitable chain-like alkoxyalkyl groups include a 1-ethoxyethyl group, 1-ethoxymethyl group, 1-methoxymethylethyl group, 1-methoxymethyl group, 1-isopropoxyethyl group, 1-methoxypropyl group, 1-ethoxypropyl group, and 1-n-butoxyethyl group.

Examples of suitable tertiary alkyloxycarbonyl groups include a tert-butyloxycarbonyl group and tert-amyoxy carbonyl group.

Examples of suitable tertiary alkyl groups include chain-like tertiary alkyl groups such as a tert-butyl group and tert-amyl group, and tertiary alkyl groups that include an aliphatic polycyclic group such as a 2-methyladamantyl group and 2-ethyladamantyl group.

Examples of suitable tertiary alkoxy carbonylalkyl groups include a tert-butyloxycarbonylmethyl group and tert-amyoxy carbonylmethyl group.

Examples of suitable cyclic ether groups include a tetrahydropyranyl group and tetrahydrofuranyl group.

Of these groups, in terms of providing excellent resolution, enhancing the uniformity of the protected material (X1), and improving the level of LER, a chain-like alkoxyalkyl group is preferred, and a 1-ethoxyethyl group or ethoxymethyl group is particularly desirable.

[0020]

Furthermore, in those cases where the protected material (X1) contains a plurality of polyhydric phenol compounds (hereafter also referred to as isomers) with differing quantities of phenolic hydroxyl groups protected with acid dissociable, dissolution inhibiting groups (different protection numbers), materials in which the protection numbers for each isomer are close in value produce superior effects for the present invention, and are consequently preferred.

[0021]

The proportion of the protected material (X1) within the base material for the pattern-forming material is preferably greater than 40% by weight, even more preferably greater than 50% by weight, even more preferably greater than 80% by weight, and is most preferably 100% by weight.

[0022]

<Unprotected Material (X2)>

The unprotected material (X2) is a material in which none of the phenolic hydroxyl groups of the aforementioned polyhydric phenol compound (x) are protected by acid dissociable, dissolution inhibiting groups, and in a base material for a pattern-forming material according to the present invention, the proportion of this unprotected

material (X2) must be no higher than 60% by weight. This proportion of the unprotected material (X2) is preferably as small as possible, and is even more preferably no higher than 50% by weight, even more preferably 10% by weight or less, and is most preferably 0% by weight. Provided this proportion of the unprotected material (X2) is no higher than 60% by weight, the level of LER can be further reduced during pattern formation. Moreover, the resolution is also superior.

[0023]

The base material for a pattern-forming material can be produced either by first producing the protected material (X1) using a method in which either all of, or a portion of, the phenolic hydroxyl groups of either one, or two or more polyhydric phenol compounds (x) are protected with acid dissociable, dissolution inhibiting groups using known techniques, and then using gel permeation chromatography (GPC) to remove the unprotected material (X2), or protecting the unprotected material (X2) with the aforementioned acid dissociable, dissolution inhibiting groups through appropriate conditions.

Furthermore, in the protected material (X1), the protection number for each of the isomers can be adjusted by altering the conditions of the method used to effect the protection with acid dissociable, dissolution inhibiting groups.

In the base material for a pattern-forming material, the relative proportions of the protected material (X1), each of the isomers of the protected material (X1), and the unprotected material (X2) can be measured using a technique such as reverse phase chromatography.

Furthermore, from the viewpoints of resolution and the LER reduction effect, the phenolic hydroxyl group protection ratio within the base material for a pattern-forming material, that is, the proportion of phenolic hydroxyl groups that have been protected with acid dissociable, dissolution inhibiting groups relative to the combined total of phenolic hydroxyl groups that have been protected with acid dissociable, dissolution inhibiting groups and unprotected phenolic hydroxyl groups, is preferably within a range from 5 to 50 mol%, and even more preferably from 7 to 30 mol%.

[0024]

A base material for a pattern-forming material of the present invention is ideal as the base material for a positive resist composition described below.

[0025]

<< Positive Resist Composition>>

A positive resist composition of the present invention includes a base material component (A) (hereafter also referred to as the "component (A)'), which contains acid dissociable, dissolution inhibiting groups and displays increased alkali solubility under the action of acid, and an acid generator component (B) (hereafter also referred to as the "component (B)") that generates acid on exposure.

In the component (A), the action of acid generated from the component (B) by exposure causes the acid dissociable, dissolution inhibiting groups to dissociate, causing the entire component (A) to change from an alkali-insoluble state to an alkali-soluble state.

As a result, when a resist film formed from the positive resist composition is either selectively exposed during the formation of a resist pattern, or alternatively is exposed and then subjected to post exposure baking, the exposed portions of the resist shift to an alkali-soluble state, whereas the unexposed portions remain insoluble in alkali, meaning alkali developing can then be used to form a positive resist pattern.

[0026]

<Component (A)>

The component (A) is the base material for a pattern-forming material (hereafter referred to as the polyhydric phenol-based base material (A1)) of the present invention.

The quantity of the component (A) within a positive resist composition of the present invention may be altered in accordance with the film thickness of the resist to be formed. A typical quantity, expressed as a solid fraction concentration, is within a range from 3 to 25% by weight, and even more preferably from 10 to 20% by weight.

[0027]

<Component (B)>

In the present invention, the component (B) can use any of the known acid generators used in conventional chemically amplified resist compositions without any particular restrictions. Examples of these acid generators are numerous, and include onium salt-based acid generators such as iodonium salts and sulfonium salts, oxime sulfonate-based acid generators, diazomethane-based acid generators such as bisalkyl or bisaryl sulfonyl diazomethanes, poly(bis-sulfonyl)diazomethanes, and diazomethane

nitrobenzyl sulfonates, iminosulfonate-based acid generators, and disulfone-based acid generators.

[0028]

Specific examples of suitable onium salt-based acid generators include diphenyliodonium trifluoromethanesulfonate or nonafluorobutanesulfonate, bis(4-*tert*-butylphenyl)iodonium trifluoromethanesulfonate or nonafluorobutanesulfonate, triphenylsulfonium trifluoromethanesulfonate, heptafluoropropanesulfonate or nonafluorobutanesulfonate, tri(4-methylphenyl)sulfonium trifluoromethanesulfonate, heptafluoropropanesulfonate or nonafluorobutanesulfonate, dimethyl(4-hydroxynaphthyl)sulfonium trifluoromethanesulfonate, heptafluoropropanesulfonate or nonafluorobutanesulfonate, monophenyl*dimethylsulfonium* trifluoromethanesulfonate, heptafluoropropanesulfonate or nonafluorobutanesulfonate, and diphenylmonomethylsulfonium trifluoromethanesulfonate, heptafluoropropanesulfonate or nonafluorobutanesulfonate. Of these, onium salts with a fluorinated alkylsulfonate ion as the anion are preferred.

[0029]

Specific examples of suitable oxime sulfonate-based acid generators include α -(methylsulfonyloxyimino)-phenylacetonitrile, α -(methylsulfonyloxyimino)-*p*-methoxyphenylacetonitrile, α -(trifluoromethylsulfonyloxyimino)-phenylacetonitrile, α -(trifluoromethylsulfonyloxyimino)-*p*-methoxyphenylacetonitrile, α -(ethylsulfonyloxyimino)-*p*-methoxyphenylacetonitrile, α -(propylsulfonyloxyimino)-*p*-methylphenylacetonitrile, and α -(methylsulfonyloxyimino)-*p*-bromophenylacetonitrile. Of these, α -(methylsulfonyloxyimino)-*p*-methoxyphenylacetonitrile is preferred.

[0030]

Of the various diazomethane-based acid generators, specific examples of suitable bisalkyl or bisaryl sulfonyl diazomethanes include bis(isopropylsulfonyl)diazomethane, bis(*p*-toluenesulfonyl)diazomethane, bis(1,1-dimethylethylsulfonyl)diazomethane, bis(cyclohexylsulfonyl)diazomethane, and bis(2,4-dimethylphenylsulfonyl)diazomethane.

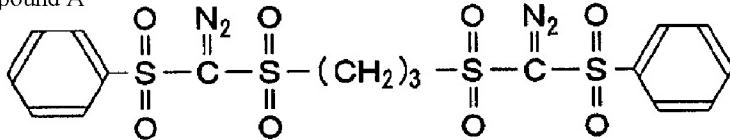
Furthermore, specific examples of poly(bis-sulfonyl)diazomethanes include the structures shown below, such as 1,3-bis(phenylsulfonyldiazomethylsulfonyl)propane (compound A, decomposition point 135°C), 1,4-bis(phenylsulfonyldiazomethylsulfonyl)butane (compound B, decomposition point

147°C), 1,6-bis(phenylsulfonyldiazomethylsulfonyl)hexane (compound C, melting point 132°C, decomposition point 145°C), 1,10-bis(phenylsulfonyldiazomethylsulfonyl)decane (compound D, decomposition point 147°C), 1,2-bis(cyclohexylsulfonyldiazomethylsulfonyl)ethane (compound E, decomposition point 149°C), 1,3-bis(cyclohexylsulfonyldiazomethylsulfonyl)propane (compound F, decomposition point 153°C), 1,6-bis(cyclohexylsulfonyldiazomethylsulfonyl)hexane (compound G, melting point 109°C, decomposition point 122°C), and 1,10-bis(cyclohexylsulfonyldiazomethylsulfonyl)decane (compound H, decomposition point 116°C).

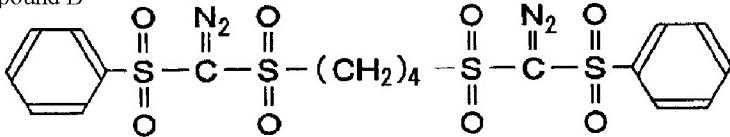
[0031]

[Formula 3]

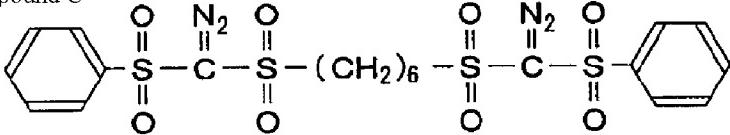
Compound A



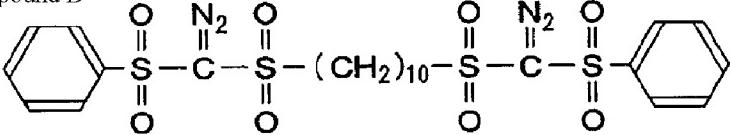
Compound B



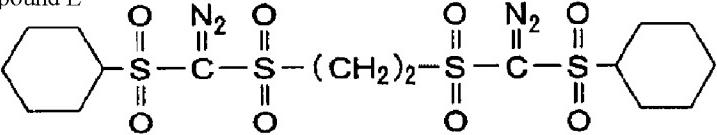
Compound C



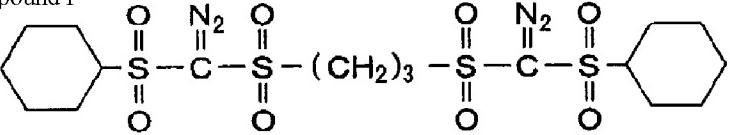
Compound D



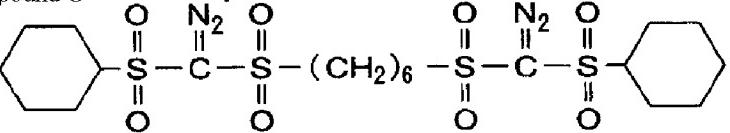
Compound E



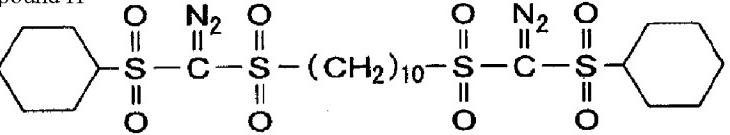
Compound F



Compound G



Compound H



[0032]

As the component (B), either a single acid generator may be used alone, or a combination of two or more different acid generators may be used.

The quantity used of the component (B) is typically within a range from 0.5 to 30 parts by weight, and preferably from 1 to 10 parts by weight, per 100 parts by weight of the component (A). At quantities less than the above range, there is a danger that pattern formation may not proceed satisfactorily, whereas if the quantity exceeds the above range, achieving a uniform solution becomes difficult, and there is a danger of a deterioration in the storage stability.

[0033]

<Organic Solvent (C)>

A positive resist composition of the present invention can be produced by dissolving the aforementioned component (A) and component (B), and each of the optional components described below in an organic solvent (C).

The organic solvent (C) may be any solvent capable of dissolving each of the components used to generate a uniform solution, and either one, or two or more solvents selected from known materials used as the solvents for conventional chemically amplified resists can be used.

Suitable examples include -butyrolactone; ketones such as acetone, methyl ethyl ketone, cyclohexanone, methyl isoamyl ketone and 2-heptanone; polyhydric alcohols and derivatives thereof such as ethylene glycol, ethylene glycol monoacetate, diethylene glycol, diethylene glycol monoacetate, propylene glycol, propylene glycol monoacetate, dipropylene glycol, or the monomethyl ether, monoethyl ether, monopropyl ether, monobutyl ether or monophenyl ether of dipropylene glycol monoacetate; cyclic ethers such as dioxane; and esters such as methyl lactate, ethyl lactate (EL), methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, ethyl pyruvate, methyl methoxypropionate, and ethyl ethoxypropionate.

These organic solvents (C) may be used either alone, or as a mixed solvent of two or more different solvents.

Furthermore, a mixed solvent formed by mixing propylene glycol monomethyl ether acetate (PGMEA) and a polar solvent is preferred, and the mixing ratio can be determined on the basis of the co-solubility of the PGMEA and the polar solvent, but is preferably within a range from 1:9 to 98:42, and even more preferably from 2:8 to 85:25.

More specifically, in those cases where EL is added as the polar solvent, the weight ratio of PGMEA:EL is preferably within a range from 2:8 to 85:25, and even more preferably from 3:7 to 74:36.

Furthermore, as the organic solvent (C), a mixed solvent of at least one of PGMEA and EL, together with -butyrolactone is also preferred. In such cases, the mixing ratio is set so that the weight ratio between the former and latter components is preferably within a range from 70:30 to 95:5.

There are no particular restrictions on the quantity used of the organic solvent (C), which is set in accordance with the coating film thickness so as to produce a concentration that enables favorable application to a substrate or the like, and is typically sufficient to produce a solid fraction concentration within the resist composition of 2 to 20% by weight, and preferably from 5 to 15% by weight.

[0034]

<Component (D)>

In a positive resist composition of the present invention, in order to improve the resist pattern shape and the post exposure stability of the latent image formed by the pattern-wise exposure of the resist layer, a nitrogen-containing organic compound (D) (hereafter referred to as the component (D)) can be added as an optional component.

A multitude of these organic compounds have already been proposed, and any of these known compounds can be used as the component (D), although an amine, and particularly a secondary lower aliphatic amine or tertiary lower aliphatic amine is preferred.

Here, an aliphatic amine refers to an alkyl or alkyl alcohol amine of no more than 15 carbon atoms, and examples of these secondary and tertiary amines include trimethylamine, diethylamine, triethylamine, di-n-propylamine, tri-n-propylamine, tripentylamine, tri-n-octylamine, diethanolamine, and triethanolamine. Of these, tertiary alkanolamines such as triethanolamine, ~~and tertiary alkyl amines such as tri-n-octylamine are~~ is particularly preferred.

These compounds can be used either alone, or in combinations of two or more different compounds.

The component (D) is typically used in a quantity within a range from 0.01 to 5.0 parts by weight per 100 parts by weight of the component (A).

[0035]

<Component (E)>

Furthermore, in order to prevent any deterioration in sensitivity caused by the addition of the above component (D), and improve the resist pattern shape and the post exposure stability of the latent image formed by the pattern-wise exposure of the resist layer, an organic carboxylic acid, or a phosphorus oxo acid or derivative thereof (E) (hereafter referred to as the component (E)) can also be added as another optional component. The component (D) and the component (E) can be used in combination, or either one can also be used alone.

Examples of suitable organic carboxylic acids include malonic acid, citric acid, malic acid, succinic acid, benzoic acid, and salicylic acid.

Examples of suitable phosphorus oxo acids or derivatives thereof include phosphoric acid or derivatives thereof such as esters, including phosphoric acid, di-n-butyl phosphate and diphenyl phosphate; phosphonic acid or derivatives thereof such as esters, including phosphonic acid, dimethyl phosphonate, di-n-butyl phosphonate, phenylphosphonic acid, diphenyl phosphonate, and dibenzyl phosphonate; and phosphinic acid or derivatives thereof such as esters, including phosphinic acid and phenylphosphinic acid, and of these, phosphonic acid is particularly preferred.

The component (E) is typically used in a quantity within a range from 0.01 to 5.0 parts by weight per 100 parts by weight of the component (A).

[0036]

<Other Optional Components >

Other miscible additives can also be added to a positive resist composition of the present invention according to need, and examples include additive resins for improving the performance of the resist film, surfactants for improving the ease of application, dissolution inhibitors, plasticizers, stabilizers, colorants, and halation prevention agents.

Examples of suitable additive resins include those resins proposed as base resins for conventional chemically amplified KrF positive resist compositions and ArF positive resist compositions, and these resins can be selected appropriately in accordance with the type of exposure light source used during resist pattern formation. The proportion of these additive resins must be kept within a range that does not impair the effects of the present invention, and is preferably no higher than 20% by weight, and even more

preferably 10% by weight or less, relative to the total solid fraction of the positive resist composition.

[0037]

<<Method of Forming Resist Pattern>>

Using a positive resist composition of the present invention, a resist pattern can be formed using, for example, the type of resist pattern formation method described below.

Namely, a positive resist composition described above is first applied to the surface of a substrate such as a silicon wafer using a spinner or the like, a prebake is conducted under temperature conditions of 80 to 150°C for 40 to 120 seconds, and preferably for 60 to 90 seconds, and the resulting film is then subjected to selective exposure with an electron beam or extreme ultraviolet radiation or the like, using an electron beam lithography apparatus or the like. In other words, following exposure through a mask pattern or patterning of the resist film by direct irradiation with an electron beam without using a mask pattern, PEB (post exposure baking) is conducted under temperature conditions of 70-80 to 150°C for 40 to 500-120 seconds, and preferably for 60 to 400-90 seconds. Subsequently, developing is conducted using an alkali developing solution such as a 0.1 to 10% by weight aqueous solution of tetramethylammonium hydroxide. In this manner, a resist pattern that is faithful to the mask pattern can be obtained.

An organic or inorganic anti-reflective film may also be provided between the substrate and the applied layer of the resist composition.

There are no particular restrictions on the wavelength of radiation used for the exposure, and an ArF excimer laser, KrF excimer laser, F₂ excimer laser, or other radiation such as EUV (extreme ultraviolet), VUV (vacuum ultraviolet), EB (electron beam), X-ray or soft X-ray radiation can be used. A positive resist composition according to the present invention is particularly useful for irradiation using EB and EUV, and especially for EB.

[0038]

As described above, a positive resist composition containing as a base component, a base material for a pattern-forming material according to the present invention, and a

polyhydric phenol-based base material (A1) enables the formation of a fine pattern with reduced LER and a high level of resolution.

The reasons for the reduction in LER are not entirely clear, but the following reasons are conceivable. Namely, roughness within the resist film surface (LER) generated during formation of the resist pattern may be caused by variations in the solubility within the alkali developing solution of the matrix molecules that constitute the base component of the resist film ,as described in 1 and 2 below.

1. In a base material containing matrix molecules with alkali-soluble groups that are either partially or completely protected with acid dissociable, dissolution inhibiting groups, variations in the alkali solubility of the base material itself can be caused by factors such as the number of acid dissociable, dissolution inhibiting groups within each matrix molecule, the number of unprotected alkali-soluble groups, and the breadth of the molecular weight distribution (the dispersity) for each of the matrix molecules.

2. Variations in the deprotection reaction that occurs during exposure and causes dissociation of the acid dissociable, dissolution inhibiting groups attached to the chemically amplified alkali-soluble matrix.

[0039]

Based on the above observations, control of at least factor 1 of the reasons described above is very difficult using the types of polymers that have conventionally been used as the base materials of resists. In other words, because polymers are obtained using methods such as polymerization, achieving a uniform molecular weight for the product polymer is extremely difficult. Although living polymerization is a process that enables a polymer with a comparatively uniform molecular weight distribution to be obtained, in order to conduct a living polymerization, various restrictions must be applied to factors such as the skeleton of the monomer being used and the polymerization solvent, and in practice, achieving a polymer of uniform molecular weight is difficult. Moreover, the polymers typically used in pattern-forming materials are usually copolymers produced using two or more monomers with different functionalities in terms of structure and alkali solubility and the like, and introducing monomers with different side-chain structures into each copolymer in a uniform manner, that is, ensuring a complete match in terms of the monomer composition within each copolymer molecule within the

product copolymer, and ensuring a uniform distribution of each monomer within each copolymer molecule is extremely difficult.

In this manner, it is thought that because a polymer in which the molecular weight distribution and the monomer composition ratio are non-uniform when viewed at the micro level is used as the base material of the pattern-forming material, a variety of problems arise during the lithography process. For example, in the spin coating step for forming the resist film, highly hydrophilic polymers and highly hydrophobic polymers form their own respective domains, or the degree to which the dissociation (the deprotection reaction) of the acid dissociable, dissolution inhibiting groups caused by the acid proceeds at the interface between the exposed portions and the unexposed portions is not uniform, meaning variations develop in the alkali solubility of each polymer molecule following the deprotection reaction, and variations also develop in the dissolution rate of the resist film.

Any such small differences in the solubility of each polymer within the resist causes an increase in the level of LER. Accordingly, in order to reduce the level of LER, the alkali solubility behavior of each polymer must be controlled, but as described above, achieving uniform alkali solubility within the polymer itself is difficult, meaning reducing the level of LER is also problematic.

[0040]

Furthermore, in the case of the low molecular weight materials proposed in the aforementioned patent references 1 and 2, it is thought that although the fact that the root mean squared radius is smaller than that of a polymer should suppress any increase in LER, absolutely no consideration is given to the difference in alkali solubility between the protected material and the unprotected material, meaning the level of LER was unable to be satisfactorily reduced.

[0041]

In contrast, a base material for a pattern-forming material of the present invention includes a protected material (X1), which is formed from a polyhydric phenol compound (x) with a molecular weight that falls within a specific range by protecting the phenolic hydroxyl groups (the alkali-soluble groups) with acid dissociable, dissolution inhibiting groups, wherein the proportion of an unprotected material (X2) is no more than a

predetermined quantity, and as a result, the overall alkali solubility is comparatively uniform, and it is thought that this uniformity is the reason for the improvement in LER.

Furthermore, the low molecular weight compounds incorporated within the base materials for pattern-forming materials have a low molecular weight that falls within a specific range, and consequently even if the protection number for the alkali-soluble groups within a single molecule is small, an adequate protection number is still achieved across the total base material, meaning a satisfactory level of dissolution contrast following exposure can still be achieved, and moreover, the resolution also improves.

In addition, the present invention also yields an improvement in the level of defects (developing defects), which represent a significant problem in conventional lithography processes. In other words, defects can appear in many different forms and for a variety of reasons, but the existence within the resist composition, and more specifically within the base material, of polymers with dramatically different dissolution behaviors is acknowledged as one primary cause. In the case of the types of polymer systems used in conventional resists, it is thought that polymers containing a high proportion of a monomer having non-acid dissociable, dissolution inhibiting groups with no alkali solubility undergo extremely little variation in polarity even under the action of acid in the exposed portions, and either appear as developing residues, or alternatively, may be dissolved during the developing process as a result of the dissolution of the surrounding polymers, but then precipitate out during the subsequent pure water rinse process and adhere to the surface of the resist thin film.

However in the present invention, as described above, the alkali solubility of each of the molecules within the material is comparatively uniform, and it is thought that this uniformity also leads to an improvement in the level of defects.

[EXAMPLES]

[0042]

As follows is a description of examples of the present invention, although the present invention is in no way limited by these examples.

[Production Example 1]

10 g of the polyhydric phenol compound represented by the above formula (II) (molecular weight: 981, hereafter abbreviated as MBSA) was dissolved in 33 g of tetrahydrofuran, 1.8 g of ethyl vinyl ether was added, and the resulting mixture was

reacted for 12 hours at room temperature under constant stirring. Following completion of the reaction, the product was extracted and purified using a water/ethyl acetate system, yielding 10.1 g of a base material for a pattern-forming material (a1).

[0043]

Using a 400 MHz proton NMR apparatus manufactured by JEOL Ltd., the number of phenolic hydroxyl groups within the base material for a pattern-forming material, and the number of phenolic hydroxyl groups protected with 1-ethoxyethyl groups were measured, and when the protection ratio (mol %) within the base material for a pattern-forming material was calculated, a protection ratio of 19.9 mol% was obtained.

The protection ratio is represented by: {number of phenolic hydroxyl groups protected with 1-ethoxyethyl groups / (number of phenolic hydroxyl groups + number of phenolic hydroxyl groups protected with 1-ethoxyethyl groups)} × 100.

Furthermore, using a high performance liquid chromatography apparatus (HP-1100, manufactured by Agilent Technologies Inc.), the respective abundance ratios (%) by weight) of unprotected material in which none of the 6 phenolic hydroxyl groups of the MBSA have been protected, 1-protected materials in which one of the phenolic hydroxyl groups is protected, 2-protected materials in which two of the phenolic hydroxyl groups are protected, and other protected materials (3- to 6-protected materials) were measured.

The results are shown in Table 1.

[0044]

[Production Example2]

With the exception of altering the quantity of the ethyl vinyl ether from the production example 1, essentially the same method was used to add the ethyl vinyl ether to the MBSA, thus yielding a base material for a pattern-forming material (a2). The protection ratio (mol %), determined in the same manner as the production example 1, was 17.1 mol%.

Furthermore, using the same high performance liquid chromatography analysis as above, the respective abundance ratios (% by weight) of unprotected material in which none of the 6 phenolic hydroxyl groups of the MBSA have been protected, 1-protected materials in which one of the phenolic hydroxyl groups is protected, 2-protected

materials in which two of the phenolic hydroxyl groups are protected, and other protected materials (3- to 6-protected materials) were measured.

The results are shown in Table 1.

[0045]

[Production Example 3]

10 g of the polyhydric phenol compound represented by the above formula (III) (molecular weight: 708, hereafter abbreviated as MBSA 2) was dissolved in 33 g of tetrahydrofuran, 4.9 g of ethyl vinyl ether was added, and the resulting mixture was reacted for 12 hours at room temperature under constant stirring. Following completion of the reaction, the product was extracted and purified using a water/ethyl acetate system, yielding a base material for a pattern forming material (a3).

[0046]

Using a 400 MHz proton NMR apparatus manufactured by JEOL Ltd., the number of phenolic hydroxyl groups within the base material for a pattern forming material, and the number of phenolic hydroxyl groups protected with 1-ethoxyethyl groups were measured, and when the protection ratio (mol %) within the base material for a pattern forming material was calculated, a protection ratio of 50.1 mol% was obtained.

The protection ratio is represented by: {number of phenolic hydroxyl groups protected with 1-ethoxyethyl groups / (number of phenolic hydroxyl groups + number of phenolic hydroxyl groups protected with 1-ethoxyethyl groups)} × 100.

Furthermore, using a high performance liquid chromatography apparatus (HP-1100, manufactured by Agilent Technologies Inc.), the respective abundance ratios (% by weight) of unprotected material in which none of the 6 phenolic hydroxyl groups of the MBSA have been protected, 1-protected materials in which one of the phenolic hydroxyl groups is protected, 2-protected materials in which two of the phenolic hydroxyl groups are protected, and other protected materials (3- to 6-protected materials) were measured.

The results are shown in Table 1.

[0047_0045]

[Example 1]

The base material for a pattern-forming material (a1) obtained in the production example 1, together with 10% by weight of triphenylsulfonium nonafluorobutanesulfonate and 1% by weight of tri-n-octylamine relative to the combined solid fraction within the base material were dissolved in a mixed solvent of ethyl lactate / propylene glycol monomethyl ether acetate = 40/60 (weight ratio), thus forming a positive resist composition solution with a solid fraction concentration of 6% by weight.

[00480046]

[Comparative Example 1]

With the exception of replacing the base material for a pattern-forming material (a1) used in the example 1 with the base material for a pattern-forming material (a2) obtained in the production example 23, a positive resist composition solution was prepared in the same manner as the example 1.

[0049]

[Example 2]

With the exception of replacing the base material for a pattern-forming material (a1) used in the example 1 with the base material for a pattern-forming material (a3) obtained in the production example 3, a positive resist composition solution was prepared in the same manner as the example 1.

[00500047]

[Evaluation Tests]

Using the positive resist compositions obtained in the examples 1 and 2, and the comparative example 1, the evaluations described below were conducted. The results are shown in Table 1. [Resolution]

Each positive resist composition solution was applied uniformly, using a spinner, to the surface of an 8-inch silicon substrate that had been treated with hexamethyldisilazane, and was then subjected to a bake treatment (PAB) at 110°C for 90 seconds, thus forming a resist film (film thickness: 150 nm). This resist film was then subjected to direct patterning with an electron beam lithography apparatus (HL-800D, manufactured by Hitachi Ltd., accelerating voltage: 70 kV), and was then subjected to a bake treatment (PEB) at 110°C for 90 seconds, developed for 60 seconds in a 2.38% by

weight aqueous solution of tetramethylammonium hydroxide (TMAH), and rinsed in pure water for 30 seconds, thus forming a line and space (L/S) pattern.

The thus obtained resist pattern was inspected using a measuring SEM, and the resolution was determined.

~~In the example 2, the conditions were altered so that the PAB was conducted at 80°C for 90 seconds and the PEB was conducted at 70°C for 300 seconds.~~

[00510048]

[Surface Roughness]

Each positive resist solution was applied uniformly, using a spinner, to the surface of an 8-inch silicon substrate that had been treated with hexamethyldisilazane, and was then subjected to a bake treatment at 110°C for 90 seconds, thus forming a resist film (film thickness: 160 nm).

This resist film was then exposed with an electron beam lithography apparatus (HL-800D, manufactured by Hitachi Ltd., accelerating voltage: 70 kV) using an exposure dose that resulted in a film thickness following developing that was approximately 90% of the initial film thickness(10 μ C/cm²), subjected to a bake treatment at 110°C for 90 seconds, and was subsequently developed in a 2.38% by weight aqueous solution of tetramethylammonium hydroxide (TMAH), and then rinsed in pure water for 30 seconds.

Following rinsing, the surface of the resist film was inspected using an AFM (atomic force microscope: DI NANOSCOPE IV/D5000, manufactured by Veeco Instruments Inc.), and the root mean squared roughness (Rms) per square μ m was determined.

[00520049]

[Table 1]

	Polyhydric phenol compound	Molecular weight	Dispersity	Protection ratio (mol%)	Abundance ratio (% by weight)			Resolution	Surface roughness
					Unprotected material	1-protected material	2-protected material		
Example 1	MBSA	981	1	19.9	41.9	18.3	20.3	19.5	50 nm L/S 1.98 nm
Comparative example 1	MBSA	981	1	17.1	80.3	3.8	4.2	11.7	80 nm L/S 2.62 nm

[00530050]

As is evident from the above results, the positive resist composition of the example 1 has a higher resolution and lower level of surface roughness than the comparative example 1, in which the abundance ratio of unprotected material exceeded 60% by weight. Even though the comparative example 1 has a protection ratio for the overall base material for a pattern-forming material that is similar to that of the example 1, the resolution was lower, and the surface roughness was larger.

~~In the example2, because a base material for a pattern forming material with a low abundance ratio of unprotected material was used, the surface roughness was extremely small.~~

The existence of a positive correlation between surface roughness and pattern LER has already been noted by Yamaguchi et al. (for example, see T. Yamaguchi et al., J. Photopolymer Sci. Technol., 10 (1997), 635), and consequently, from the above results it is evident that the LER is very favorable for the patterns obtained using the positive resist compositions of the examples 1 and2. Furthermore, the improvement in the surface roughness of the rinsed resist film can be expected to also provide an improvement in the level of defects.

[Name of Document] Abstract

[Abstract]

[Problems to be Solved by the Invention] To provided a base material for a pattern-forming material, a positive resist composition, and a method of resist pattern formation that are capable of forming a pattern with reduced levels of LER.

[Means for Solving the Problems] A base material for a pattern-forming material, comprising a protected material (X1), which is formed from a polyhydric phenol compound (x) that comprises two or more phenolic hydroxyl groups and has a molecular weight within a range from 300 to 2,500, in which either a portion of, or all of, said phenolic hydroxyl groups are protected with acid dissociable, dissolution inhibiting groups, wherein a proportion within said base material of an unprotected material (X2), in which said phenolic hydroxyl groups of said polyhydric phenol compound (x) are not protected with acid dissociable, dissolution inhibiting groups, is no more than 60% by weight.

[Selected Figure] None

Historical Information on Applicant

Identification Number [000220239]

1. Date of Change August 30, 1990

[Reason for Change] New Registration

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